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Evaluation of the corrosion resistance of Ni(P)Cr coatings for bipolar plates by electrochemical impedance spectroscopy

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1. Introduction

Bipolar plates (BPs) are one of the key elements in PEM fuel cells. Among other functions, they homogeneously distribute the reactant gases inside the cell, facilitate the elimination of water and excess heat, and transport the generated current cell by cell to the external load. To fulfill all these missions, plate materials must combine a high thermal and electric conductivity, surface hydrophobic character and a good resistance to corrosion [1]. The relative increase in the internal ohmic resistance over time observed in PEMFC is caused by irreversible processes, such as degradation phenomena. They are responsible of a performance deterioration and an abrupt shortening in the lifetime of these electrochemical devices. In the present research, corrosion phenomena in NiPCr coatings for aluminum BPs are analyzed. Different experimental techniques such as scanning electron microscopy, energy-dispersive X-ray spectroscopy and x-ray diffraction were employed for the microstructure and morphology characterization. On the other hand, electrochemical impedance spectroscopy (EIS) was used as a diagnostic tool to study the corrosion. EIS allows obtaining an equivalent circuit with electronic passive elements, representative of the physical system under study, useful to study the corrosion behaviour as a function of time, and to evaluate the surface degree of protection provided by the coating.

2. Experimental

2.1 Preparation of the samples

Two types of coatings were applied on AA7075-T6 aluminium (Al) substrates [2]. Electroless Ni(P) single coatings 20 µm, 40 µm and 60 µm thick were applied to samples that are indentified as NiP20, NiP40 and NiP60, respectively. Ni(P)Cr double coatings (30 µm) were also tested. In this case, a first electroless Ni(P) layer, was combined with second Cr layer deposited over it by electroplating.

2.2 Microstructure and Morphology

Surface morphology and cross-section images of Ni(P) and Ni(P)Cr were observed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The structure of these coatings was assessed by x-ray diffraction (XRD).

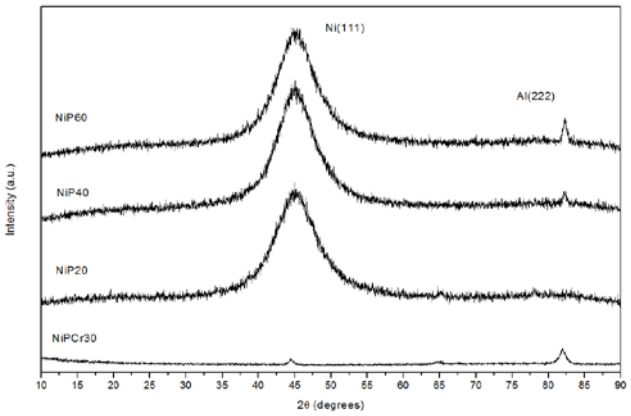
2.3 Electrochemical corrosion tests

Corrosion tests were performed with a three-electrode corrosion cell, using one of them as reference. The reference and counter electrodes were Ag/AgCl (+0,207 V vs SHE) and a platinum sheet, respectively. Ni(P) and Ni(P)Cr Al-coated samples were the working electrodes. A solution of H_2SO_4 + 0.1 ppm HF (pH 3) at 80 °C saturated with N_2 was used as electrolyte, simulating anodic conditions. Potentiostatic polarization tests (PPTs) were carried out at +600 mV. After the PPTs, the samples were settled for 5 min to attain its stable open circuit potential, OCP. Then, electrochemical impedance spectroscopy (EIS) measurements were performed. Impedance data were collected for frequencies ranging from 10 mHz to 100 kHz with an excitation amplitude of 10 mV, using a PARSTAT 2273 potentiostat. The impedance data were curve-fitted to equivalent circuits using Zview software (Scribner).

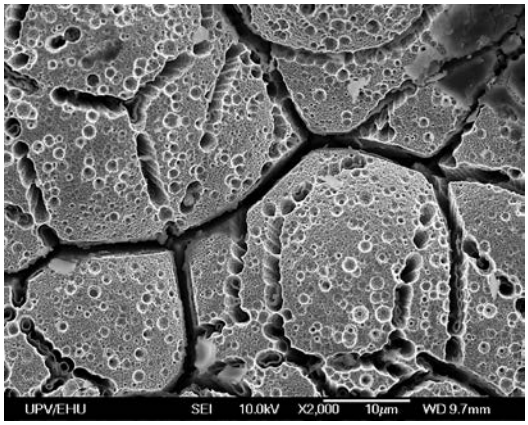
3. Results and Discussion

3.1 Characterization of Ni(P)Cr coatings

X-ray diffraction patterns of Ni(P)Cr coatings are shown in Figure 1a. In the NiP20, NiP40 and NiP60 samples, a broad peak centered around 45º is observed, which indicates the presence of amorphous and nanocrystalline Ni, textured in Ni (111), with a crystal size lower than 2 nm. The surface of the NiPCr30 Al coated sample has a crystal size of 10-15 nm. The metal substrate (AA7075-T6) appears at 82º (except for NiP20 sample), textured at (222).



a)



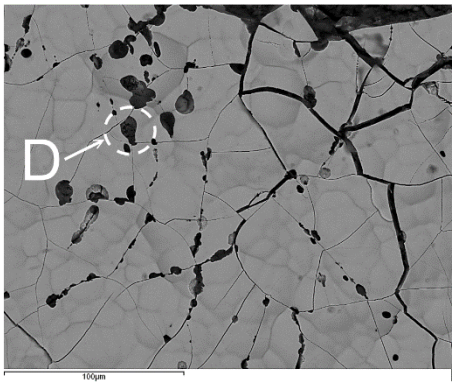
b)

Figure 1. a) XRD patterns of the Ni(P) and Ni(P)Cr coatings. b) SEM image of the Ni(P)20 surface coating after PPTs (5 h).

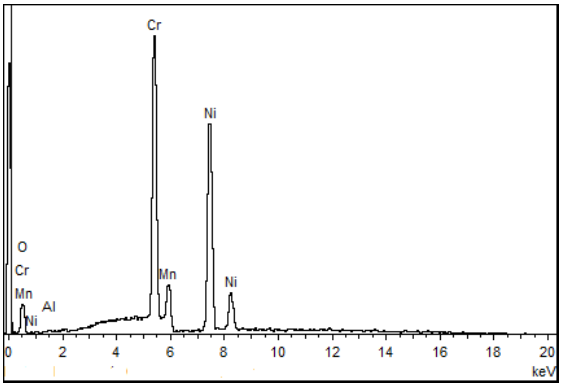
3.2 Potentiostatic polarization

Fig. 1b shows a SEM image of the surface morphology of an electroless NiP20 coating after PPTs. Ni(P) coatings exibit a typical cauliflower-like morphology with a smooth surface before PPTs. During PPTs, the long and straight boundaries around the cauliflower-like deposited grains act as appropiate corrosion paths [3], as can be seen in Fig. 1b. The underlying substrate (Al) will be attacked due to galvanically induced corrosion (Al being the anode and Ni(P) being the cathode) as soon as the coating layer is perforated [4]. Al and O were detected by EDX in delaminated areas of the Ni(P) coatings, which indicates that corrosion has reached the aluminiun substrate.

On the other hand, in Ni(P)Cr doble layer coatings, the chromium oxide layer acts as barrier in the growth of corrosion paths, improving the corrosion resistance (Fig. 2a). In this case only the local chromium coating defects form direct paths between the corrosive environment and the underlaying Ni(P) coating. Ni and O were detected by EDX in these coating deffects as depicted in Fig. 2b.



a)

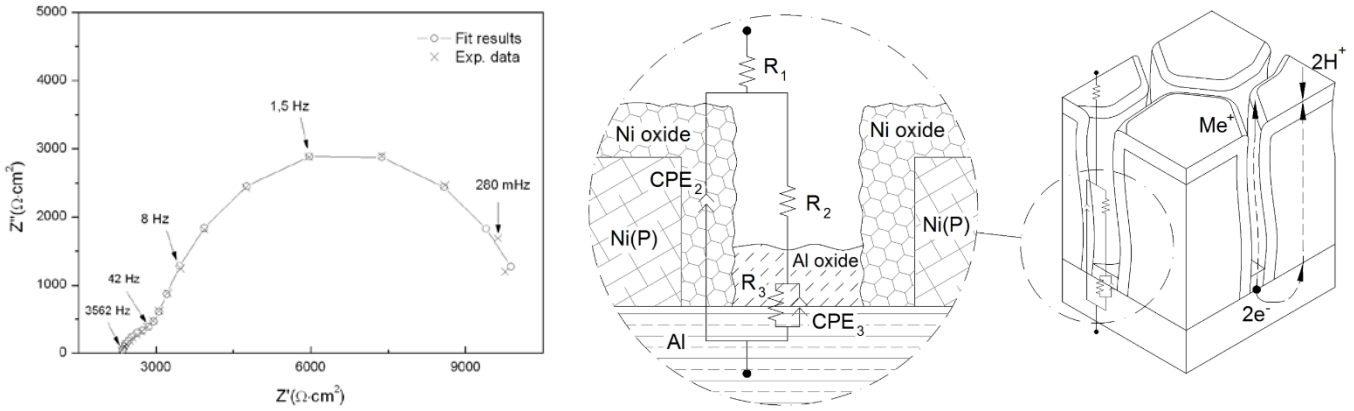


b)

Figure 2. a) SEM image of a NiPCr coating. b) EDX spectra of the defect identified by “D”.

3.3 Electrochemical Impedance Spectroscopy (EIS)

Fig. 3a shows a representative Nyquist plot and the fitted results for the Ni(P) coating samples after PPT at +600mV. The Nyquist semicircles confirm the two time constants behaviour. The first relaxation process is related to the coating layer and is reflected in the higher frequencies ($R_2 \cdot CPE_2$), whereas the second relaxation process ($R_3 \cdot CPE_3$), observed at the lower frequencies, represents the electrochemical behaviour at the interface between the substrate and the coating. The equivalente circuit used to analyze the EIS measured spectra for both the NiP and NiPCR coatings is depicted in Fig. 3b. The circuit includes the solution resistance (R_1), and the high (Hf) and low (Lf) frequency time constants. The Hf corresponds to the coated areas and can be represented by the pore resistance (R_2) and the coating capacitance (CPE_2). The Lf is assigned to the polarization resistance (R_3) and the double layer capacitance (CPE_3). The constant phase elements (CPE) simulate the non-ideal behaviour of the capacitance, and are indicative of the surface roughness [5]. The polarization resistance of the coating, Rp, is calculated as the sum of R_2 and R_3.and It decreases, in both coatings, as the PPT time increases.



a) b) c)

Figure 3. a) Nyquist plot of a NiP20 coated sample after 10 min of PPT at +600mV (vs Ag/AgCl), b) equivalent circuit obtained from EIS, and (c) galvanic corrosion in the pores.

Conclusions

Electrochemical Impedance Spectroscopy (EIS) has proved to be a powerful technique to study the corrosion behaviour of protective coatings for BPs. An equivalent circuit has been proposed that accurateky fits the impedance spectra for both, NiP and NiPCr coatings. Chromium raises the total Rp value of the coatings, due to the blockage of the Ni(P) substrate boundary grains. When the coating layer is perforated, corrosion of the metal base becomes severe, eventually breaking the nickel protective film.

Acknowledgements

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